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Comprehensive Study of Polychlorinated Naphthalene Compounds in Materials and Products: Review

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Abstract

Polychlorinated naphthalenes (PCNs) consist of 75 potential congeners in eight homologous groups. PCNs are toxic, resist decomposition, and bioaccumulate in adipose tissue. They are transported through air, water, and migratory birds, across international borders and precipitate far from place. Released, where they accumulate in terrestrial and aquatic ecosystems, PCNs form as unintended persistent organic pollutants (UPOPs) with PCDDs, PCDFs, PCBs, and other UPOPs. Polychlorinated naphthalenes are used in multiple applications such as chlorine rubber, pyrene, sealants or adhesives, and in similar applications such as capacitors, transformers, and anti-corrosion paints. They have innumerable uses and applications, and thus representing an imminent environmental danger to Earth and humans. States and those with an interest in the seriousness of naphthalene may also consider an approach developed for the inventory of naphthalene. There are many different methods that have been used to collect information for POPs inventories, such as the indicative method, the qualitative method, and the quantitative method. This study explains their nature, sources, physical and chemical properties, products that may contain them, steps and stages of PCN control in products and tools, and the most important in this review, that it explains the methods of sampling, screening and analysis of PCNs in water, air, soil and in different products.

Keywords: *polychlorinated naphthalenes, properties, sampling, screening, analysis methods.*

1. Introduction

Historically, PCBs and PCTs have been found in different closed ad open locations. They may present in completely closed or nominally closed systems, they are found in electrical utilities such as transformers, capacitors, switches, voltage regulators, circuit breakers, and light ballasts. Also waste electrical or electronic equipment, containing small capacitors and cables.Furthermore they are found in industrial facilities, railway systems and installations like transformers, capacitors, voltage regulators, circuit breakers, lighting ballasts, heat transfer fluids, hydraulic fluids, earthing coils. Additionally,they may present in research laboratories tools like vacuum pumps, lighting ballasts, capacitors, and circuit breakers. Also in sewage disposal facilities such as vacuum pumps, well engines, and in car service stations: reused oil. As for their presence in open systems, it includes residential commercial buildings, rubber joints and filters, sealant glue, paints, concrete, and gypsum. Also in steel structures such as bridges, tanks, paints and coatings laying pipes. Besides the industrial production of PCBs, there is also the release of PCBs into the environment by commercial PCB products, where PCNs are present as secondary pollutants [1]. PCNs are also formed in various combustion [2][3] and industrial processes such as the production of magnesium [4] and copper [5][6].

2. Polychlorinated naphthalenes (PCNs)

Chlorinated naphthalene includes 75 similar compounds within eight homologous groups containing one to eight chlorine atoms distributed on the plane surface of the aromatic naphthalene molecule. The primary structure of PCNs is shown in Figure (1) and has the molecular formula $C_{10}H_{8-n}Cl_n$, where n = 2-8. And the study covered by this research is concerned with the analysis and sampling of chlorinated naphthalene from a compound of polychlorinated naphthalenes, i.e. dichlorinated naphthalenes, trichlorinated naphthalenes, tetrachlorinated naphthalenes, pentachlorinated naphthalenes, hexachlorinated naphthalenes, heptachlorinated naphthalenes and octachlorinated naphthalenes. Figure (2) and table (1) shows these naphthalenes.

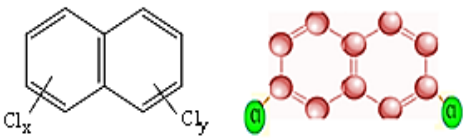

Figure (1): General composition of polychlorinated naphthalene (PCNs)

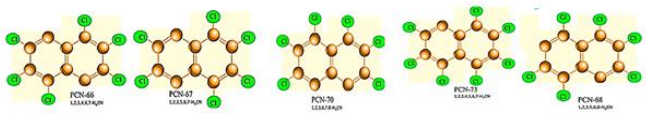

Figure (2): Structural structure of some polychlorinated naphthalenes [7]

Table **1**: Names and CAS numbers for PCNs homologue groups (NICNAS 2002)

PCNs name	CAS number	Molecular formula
(*Monochloronaphthalene*)	25586-43-0	$C_{10}H_7Cl$
Dichloronaphthalene	28699-88-9	$C_{10}H_6Cl_2$
Trichloronaphthalene	1321-65-9	$C_{10}H_5Cl_3$
Tetrachloronaphthalene	1335-88-2	$C_{10}H_4Cl_4$
Pentachloronaphthalene	1321-64-8	$C_{10}H_3Cl_5$
Hexachloronaphthalene	1335-87-1	$C_{10}H_2Cl_6$
Heptachloronaphthalene	32241-08-0	$C_{10}HCl_7$
Octachloronaphthalene	2234-13-1	$C_{10}Cl_8$

3. Sources of polychlorinated naphthalenes

PCNs are unintentionally generated during industrial processes that use high temperature (particularly waste incineration as well as in other processes known to generate PCDDs and PCDFs). PCNs are released in an unknown amount from waste disposal sites and old tool stocks. PCNs in PCBs are mainly formed along with PCBs (ie at disposal sites for PCBs and in PCBs-containing equipment). Figure(3) shows overview of initial PCN substance flow.

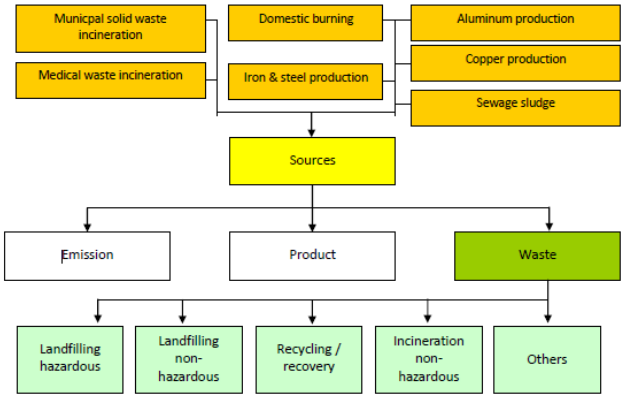

Figure (3): Overview of initial PCN substance flow

4. Physical and chemical properties of the various isoforms

The physical and chemical properties vary greatly due to the degree of chlorine substitution. Chlorinated naphthalenes from Trichloro to Octachlor are highly lipid soluble with a high octanol partition coefficient (>5). The values of the octanol partition coefficient have been experimentally determined in the following table, while annex I of document UNEP/POPS/POPRC.8/16/Add.1 contains modeled values for the quantitative relationship between structure and activity (properties) [9]. The modeled values were lower for similar compounds with higher chlorine content. The solubility in water and vapor pressure decrease as the degree of chlorination decreases. Dichlorinated naphthalenes have a slightly lower water solubility, while higher chlorinated naphthalenes have a water solubility of a few mg/L. For chemicals with lower solubility in water, the measured values show a higher degree of uncertainty [10]. Posen [11] and others in (2009) developed a model for the quantitative relationship between structure and properties in order to evaluate solubility in water, octanol and water partition coefficient, octanol partition coefficient, water partition coefficient and Henry's law constant for all 75 similar compounds. The water solubility estimates were lower than the values presented in Table (2). The values for these modeled end points are also included in Annex I of document UNEP/POPS/POPRC.8/16/Add.1. Table (2) provides a summary of the range of the octanol and water partition coefficients for the different isoforms. While in the gaseous phase, PCNs bind to molecules due to their semi-volatile nature. Based on Henry's law constant, volatilization from moist soil and water surfaces is expected for PCNs, from dichlorinated naphthalenes to hexachlorinated naphthalenes. The UV spectrum of PCNs shows maximum strong absorption values between 220 and 275 nm, and lower maximum values between 275 and 345 nm. The maximum values of absorption tend towards higher wavelengths as the degree of chlorination increases (according to Brinkmann and Reimer, 1976 [12], according to Jacobson [13] and Aspland, 2000 references).

5. Products and materials possibly containing PCNs

PCNs were produced and used as commercial mixtures mainly between 1920 and 1970, and some companies used PCNs in products until around 2000.[14][15] The total commercial production of PCNs is estimated at 150,000 tons. Similar to PCBs, PCBs have been used in closed applications (such as capacitors and transformers) and in a wide variety of open applications including cable insulation and wood preservation as an additive in paints, pigment carriers, dye primers, and motor oils. And if a study is planned on the presence of PCN-containing substances, then this list can be evaluated in search of samples of possible relevance to the country. Since PCN production was largely phased out in the 1980s and 1990s, most PCN-containing goods and products have either reached the end of their life or have already been phased out. Some PCNs are unintentionally formed in the production of organochlorine chemicals and in thermal processes. Since PCBs and SCCPs (recommended for inclusion at COP8 in 2017) [16] have been used in many of these applications, examination and analysis of selected PCB samples can be combined with PCB assay. A "Draft Guidance on the Preparation of Inventories of Polychlorinated Naphthalenes (PCNs)" has been developed, proposing to each Stockholm Convention signatory this project sets out the specific Level III inventory tasks, examination and analysis of PCNs for selected materials and products in use and stock [17]. For the sampling and monitoring of PCNs in waste, reference can be made to the Basel Convention technical guidelines that consider PCNs[18].

6. Step by step approach for PCN monitoring in products and materials

Step 1: Survey of products and materials possibly containing PCNs (and PCBs)

Prior to sample collection, a survey is conducted to initially identify relevant products and items in current use or end-of-life that may contain PCNs.

Step 2: Sample collection

Samples may be collected for example by customs authorities upon import or by competent authorities such as factory control or consumer protection authorities and related institutions. Since PCNs (eg PCBs) are used in open applications such as paints and construction sealants, this sector is also suitable for evaluation and collection. Sampling campaigns may also be conducted by research institutions, possibly in collaboration with other relevant entities or directly with industry or waste management facilities. The following standards and information may be used by stakeholders:

- The product that was produced or applied during the time that PCNs were produced and used.
- CAS numbers, chemical names, or product names.
- specific risk criteria.

The procedures developed for sampling PCB oils in transformers and capacitors can be similarly applied to PCNs in these applications. Variation is the final automated analysis that can be combined with PCB analysis in these samples. For PCNs in open application, there is currently no standard method such as sampling PCNs in paints and coatings in construction or ships or PCNs in products such as cables or rubber. If monitoring of PCNs in some of these product categories is considered relevant, samples will be collected taking into account the time at which PCNs have been used in these applications.

Step 3: Screening of products in the field and in the laboratory

Samples of materials and tools can be checked for the presence of chlorine in the field or in the laboratory. Transformer and transformer oils can be tested with chlorine test kits such as the Clor-N-Oil or Dexsil test. Within these evaluations, however, this check for chlorine in capacitor or transformer oil is not specific to PCNs for all sample types since PCBs have been used in larger quantities in these applications. Since PCBs need to be evaluated in such checks, the chlorine test should be applied in any case. The "density test" of oils can be used to pre-screen the detection of pure PCN oil or PCB oil containing transformers or capacitors. PCB transformers, pure transformers containing PCN may also be tested positive because the density of PCNs is similar to that of PCBs (1.2 to 1.5). Paints, coatings, sealants or rubber may also be checked using XRF for chlorine. In this case, the sample is not chlorine positive for polychlorinated puffs. It does however indicate that the material may contain PCNs, PCBs or SCCPs, with other chlorine-containing substances such as chloroprene rubber or PVC giving a positive indication. Rapid screening methods such as GC/MS pyrolysis can be used to rapidly check for the

presence of PCNs. A simple scanning [19]assay for POP-BFRs has recently been developed in which the samples in question were processed with pre-cleaned filter paper folded into quarters, moistened with isopropanol and then wiped tightly in concentric circles toward the middle of the region. Rinsing this filter paper led to the identification of the BFRs present even in a semi-quantitative manner. This simple screening may also be possible for PCBs (and PCBs) in open applications such as paints, coatings, sealants or rubber, but they need to be evaluated. When applying screening methods, it must be ensured that the detection limit of the screening method is lower than the limit required for screening, eg required of a certain legislative limit or below the low POP content of the Basel Convention of 50 mg/kg or 10 mg/kg [20]

Table 2: Selected physical and chemical properties (UNEP 2013 based on IPCS 2001)

Congeners	Molecular weight (g/mol)	Solubility (µg/L) [a]	Vapour pressure (Pa)[b] (sub-cooled liquid, 25°C)	Henry's law constant (Pa·m³/mol, 25°C)[c]	Log K_{ow} [d]	Log K_{oa} [e]	Log K_{aw} [e]	Melting point (°C)	Boiling point (°C)
Di-CNs	197.00	137–862 (2713)	0.198–0.352	3.7–29.2	4.2–4.9	6.55 to 7.02	-2.83 to -1.98	37–138	287–298
Tri-CNs	231.50	16.7–65 (709)	0.0678–0.114	1.11–51.2	5.1–5.6	7.19 to 7.94	-3.35 to -2.01	68–133	274*
Tetra-CNs	266.00	3.7–8.3 (177)	0.0108–0.0415	0.9–40.7	5.8–6.4	7.88 to 8.79	-3.54 to -2.02	111–198	Unknown
Penta-CNs	300.40	7.30 (44)	0.00275–0.00789	0.5–12.5	6.8 - 7.0	8.79 to 9.40	-3.73 to -2.3	147–171	313*
Hexa-CNs	335.00	0.11* (11)	0.00157–0.000734	0.3–2.3	7.5 - 7.7	9.62 to 10.17	-4.13 to -3.04	194	331*
Hepta-CNs	369.50	0.04* (2.60)	2.78 x 10-4, 2.46 x 10-4	0.1–0.2	8.2	10.68 to 10.81	-4.34 to -4.11	194	348*
Octa-CN	404.00	0.08 (0.63)	1.5 x 10-6	0.02	6.42–8.50	11.64	-5.21	198	365*

Table 3: Trade names, composition and manufacturers of technical PCN mixtures* (IPCS 2001).

Trade name		Approximate composition	Manufacturer
Halowax	1031	mono-diCN (22% Cl)	**Koppers Co Pittsburg, PA, USA**
	1000	mono-diCN (26% Cl)	
	1001	di-penta (50% Cl)	
	1099	di-pentaCN (52% Cl)	
	1013	tri-pentaCN (56% Cl)	
	1014	tetra-hexaCN (62% Cl)	
	1051	hepta-octaCN (70% Cl)	
Basileum	SP-70	mono-diCN (80% PCN)	**Desowag-Bayer, Germany**
Nibren wax	D88	(50% Cl, estimated from melting point)	**Bayer Leverkusen, Germany, formerly I.G. Farbenindustrie**
	D116 N	(50% Cl, estimated from melting point)	
	D130	(60% Cl, estimated from melting point)	
Seekay wax	R68	(46.5% Cl)	**ICI Runcorn, Great Britain**
	R93	(50% Cl)	
	R123	(56.6% Cl)	
	R700	(43% Cl)	
	RC93	(50% Cl)	
	RC123	(56.5% Cl)	
Clonacire wax	95	(50% Cl, estimated from melting point)	**Prodelec, Paris, France**
	115		
	130		

*Mono-CNs are not listed as POPs in the Stockholm Convention. Mono-CN products might however contain higher chlorinated PCNs listed in the Convention.

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Step 4: Quantification

Various analytical methods can be applied for the utilitarian quantification of polychlorinated waste and they have been described in previous studies [21][22].

7. Analysis and sampling

Analysis refers to the extraction, purification, separation, identification, quantification, and reporting of POPs concentrations in the substance in question. The development and dissemination of reliable analytical methods and the collection of high quality analytical data are important to understanding the environmental impact of hazardous chemicals, including persistent organic pollutants.

7-1 Screening methods for chlorine as indication for PCN

5-1-1- Screening for oils in capacitors and transformers

One of the previous major uses of PCNs was in capacitors from the 1930s to the 1980s. Since capacitors are closed applications, these capacitors will only be checked for PCNs and PCBs.

Here are the sorting steps to classify capacitors:

1. Check the year of manufacture: if it was manufactured in 1990 or later it is definitely "PCB/PCN-free."
2. Name plate check: If there is indication of presence/absence of PCN/PCB or any class accordingly.
3. If it's not clear, either find and sample and analyze a capacitor similar to it - or classify it as containing PCBs/PCNs.

To check capacitor or transformer oils for PCNs (or other chlorinated POPs used in transformers or capacitors such as PCBs or HCBD), oil check test kits such as Clor-N-Oil, Dexsil or L2000 can be PCB/Chloride Analyzer are used. Further laboratory analysis of positive samples tested for chlorine may be carried out to determine the POPs content of PCN, PCB or HCBD [23]. Density test with water can also be used for pre-screening. This test compares the density of transformer/condenser oil to water to determine the presence of PCBs or other organochlorine oil by observing whether the oil sample floats. However, when using a density test, only pure or high-contaminated transformers and capacitors (with PCN or PCB) will test positive because the density of PCNs is similar to that of PCB (1.2 to 1.5) while the density of oil contaminated with low PCBs PCBs or PCBs less than 1. XRF technology can also be used to check for organic chlorine in oils. However, the detection limit of some XRF equipment may not reach the detection limit of 50ppm of chlorine for the oil.

7-1-2-Screening of coatings, paints, rubber and cables

XRF and sliding spectroscopy can detect chlorine. The detection limit depends on the tool. For XRF, the detection limits for chlorine are higher compared to bromine. XRF is known to have a chlorine detection limit of about 100 mg/kg. XRF lab equipment can reach detection limits of 10ppm. And for sealants and chalk, XRF inspection can detect PCN and PCB-containing sealants. Additive levels in sealants typically range between 5% and 25%. [24] , Since chlorinated paraffins are also used in sealants, the detection of chlorine requires further confirmation analysis to determine the additive. In anti-corrosion coatings, PCBs and PCN additives have been used mainly in chloroprene and chloroprene paints as well as in plastic copolymers with a ratio of 5 to 35% after drying. All plastic and chloroprene coatings also give off a positive signal for chlorine using XRF or other sieving techniques not intended for PCBs or PCBs. Also for chloroprene rubber (eg neoprene FP or PVC cables, the chlorine screening is positive and does not indicate the additive used). For these samples, only instrumental analysis can reveal the relevant additive.

8. Sample preparation, extraction and clean-up

8-1 Extraction

It is difficult to extract a dielectric liquid as a sample from sealed electrical equipment such as capacitors. In this case, a small hole should be carefully drilled on the upper part of the stomach and a liquid sample taken. After the sample is taken, the hole should be closed and repaired. During sampling of shredder residues, care should be taken for the homogeneity of the sample. Samples are usually extracted by the standard method such as Soxhlet extraction. Soxhlet extract with toluene was used by Yamato et al. (2005) [25]. For a wide range of sample matrices including rubber, printer belts, ASR, derivative fuels and fly ash. Therefore, conventional extraction methods that extract OHS from highly reproducible biological matrices can also be used to analyze PCNs [26][27]. Since PCNs are planar compounds and may adsorb fairly strongly to carbon molecules, particularly effective methods are recommended for OHS extraction from the matrix, for example. Soxhlet extraction with toluene, for samples with high carbon content [28].

Types of matrices of particular interest in the analysis of PCBs, PCTs, and PBBs include:

- Used motor oils, waste oils, various fuels and other used organic fluids.
- Synthetic industrial PCBs and oil-containing PCTs from transformers or other equipment or in bulk storage
- Mineral oil from backfilled transformers contaminated with PCBs or stored in bulk.
- Flexible joints and gaskets, various types of sealant glues, and paints.

8-2 Clean-up

Depending on the matrix, different cleaning methods need to be applied perhaps using multi-layer columns or a series of cleaning columns. PCNs can be finally cleaned on an activated carbon cartridge column (eg Carboxen, Supelco) The cartridge column is washed with solvents (eg 25% dichloromethane/hexane; volume depends on column size) and PCNs are recovered by backflow with toluene. Hot (appropriately sized depending on column size) and cleaning methods have been developed to separate PCNs from PCBs due to potential interference in the analysis. Here for example silica gel-impregnated activated carbon columns can be applied [29].

8-3 Liquid chromatography

8-3-1- Gel Permeation Chromatography

Gel-permeable chromatography (GPC) has been found on styrene-divinylbenzene copolymer columns (PLgel, Polymer Laboratories) to separate PCN from PCB for example. The gel has a specific pore size of 50 microns and can also be used at high pressures. The method was first applied to isolate PCNs in commercial PCB products [30].

8-4 PYE Column

During the 1990s, the use of HPLC as well as 2-(1-pyrenyl)ethyldimethylsilylated silica (PYE) to separate planar compounds became more common,. For example, PCNs and non-ortho PCBs were separated from most PCBs using a PYE column with the use of n-hexane as the mobile phase.

8-5 Straight-Phase and Reversed-Phase Liquid Chromatography

Brinkman and Reymer (1976) have summarized the behavior of PCNs in straight phase (silica gel) and reverse phase chromatography (Inverted phase) [31].

9. Quantitative analysis of PCNs

PCNs are typically analyzed by GC-LRMS, GC-HRMS, or other GC-MS systems. PCNs can also be detected using an EDC detector.The GC-ECD can be applied to PCN samples if PCNs are major contaminants in a sample with low PCB levels. However, if PCBs are present in higher concentrations compared to PCBs (eg PCB oils and then PCN, then the combined PCBs interfere with the quantification of PCBs. For such samples, GC/MS will be required for the determination of polychlorinated naphthalenes.

9-1 Gas chromatography

Several stationary phases of GC are used to separate individual naphthalene congeners in halowax mixtures [32]. For example Iphenylmethylpolysiloxane (5%) columns are frequently used in the decomposition of polychlorinated naphthalenes, and remove the chlorinated naphthalene congeners in groups of congeners. In general, the fixed polar phases give wider retention periods for each homogeneous group. In most stationary polar phases, the different degrees of chlorination interfere with each other and the rinsing order sometimes changes [33]. To fully dissolve the chlorinated naphthalene congeners, different types of gas chromatography stationary phases are required. Using three types of cyclodextrin columns and a liquid crystal column (SB-Smectic) eight of the ten hexaCN congeners were separated [34]..Table (4) shows an example of GC/MS conditions for PCNs.

9-2 Mass Spectrometry

In order to avoid interferences from OHS drying, polychlorinated naphthalenes are preferably analyzed by gas chromatography-mass spectrometry (GC-MS). The response in negative electron capture ionization (ECNI-MS) is high for pentagonal up to octaCN, but varies greatly between homogenates. Electron ionization (EI) is thus the useful technique when several PCNs are included in the analysis. For quantitative analysis, selected ion monitoring (SIM) that detects molecular ions should be used to obtain the highest sensitivity. For samples with high levels of PCNs, low-resolution mass spectrometry (LR-MS) can be sufficient but for low levels, or when high selectivity is necessary, high-resolution mass spectrometry (HR-MS) is the preferred method [35][36] . There are several analytical difficulties associated with the accurate determination of PCNs, and current methods are similar to the analytical methods used for PCBs. It relies on carbon cleaning (from arrays) and phase fractionation followed by high-resolution chromatography, and the use of high-resolution spectrographs to know the properties of mass (HRGC/HRMS) for the minimum levels of high selectivity among PCNs. However, less than half of the potential isotropic compounds are commercially available and isotopically labeled, eg there are no 13C-labelled trichloronaphthalenes. There are currently no congeners of 13C-labeled PCNs commercially available, and therefore 13C-labeled PCBs are frequently used as internal standards for analyzing PCNs. However, it should be noted that the main hexaCNs in i.e. technical products. 1,2,4,5,6,88-hexaCN (CN-71) as well as 1,2,4,5,7,8-hexaCN (CN-72) (secondary pollutants in living organisms) are eluted in GC with 3,3¢,4,4¢,5-pentaCB (CB-126). The effective numbers of exact masses for the original PCNs and 13C are shown in the following table [37]:

Table (4): Example of an effective setup for GC/MS analysis of PCNs

GC column	**DB-5MS（Agilent Technologies/J&W）fused silica capillary column ID 0.32 mm, length 60 m, thickness 0.25 µm**
Oven Temp.	**90°C (2 min hold) - (20°C/min)→160°C - (3°C /min) →245°C -(5 C/min) →310°C（2 min hold）**
Injection	**On-column or Split less**
Injector Temp. (On-column)	**90 C(1 min hold)－（100 C/min）→300 C**
Injection volume	**1～2 Ml**
HRMS condition	**Autospec Ultima （Waters/Micromass）**
Ionization	**EI**
Ionization voltage	**35 V(35～70 V)**
Ionization current	**500 µA**
Accelerating voltage	**8 kV**
Ion source Temp.	**290～300 °C**
Interface Temp.	**290～300 °C**
MS resolution	**10 000**

Table 5 : Masses of detected ions (*m/z*'s) and isotope ratio for PCNs

	CL degree	M^+	$(M+2)^+$	$(M+4)^+$
Native PCN	*MoCNs (not listed)*	*162.0237(100)*	*164.0208(32.6)*	
	DiCNs	195.9847(100)	197.9818(64.5)	
	TrCNs	229.9457(100)	231.9428(96.5)	
	TeCNs	263.9067(77.8)	265.9038(100)	
	PeCNs		299.8648(100)	**301.8619(64.3)**
	HxCNs		333.8258(100)	**335.8229(80.3)**
	HpCNs		367.7869(100)	**369.7839(96.3)**
	OcCN		401.7479(89.1)	**403.7450(100)**
Internal Standard for PCN	$^{13}C_{10}$-DiCN	206.0183(100)	208.0152(64.0)	
	$^{13}C_{10}$-TeCNs	273.9402(78.2)	275.9373(100)	
	$^{13}C_{10}$-PeCNs		309.8983(100)	**311.8954(64.0)**
	$^{13}C_{10}$-HxCNs		343.8593(100)	**345.8564(80.0)**
	$^{13}C_{10}$-HpCN		377.8204(100)	**379.8174(95.9)**
	$^{13}C_{10}$-OcCN		411.7814(89.4)	**413.7785(100)**
	$^{13}C_{12}$-DiCB*,**	234.0406(100)	236.0376(65.6)	
	$^{13}C_{12}$-TrCB*	268.0016(100)	269.9986(98.0)	
	$^{13}C_{12}$-TeCB**	301.9626(78.2)	303.9597(100)	
	$^{13}C_{12}$-PeCB*		337.9207(100)	**339.9177(65.3)**
	$^{13}C_{12}$-HxCB*		371.8817(100)	**373.8788(81.5)**
	$^{13}C_{12}$-OcCB*		439.8038(87.8)	**441.8008(100)**

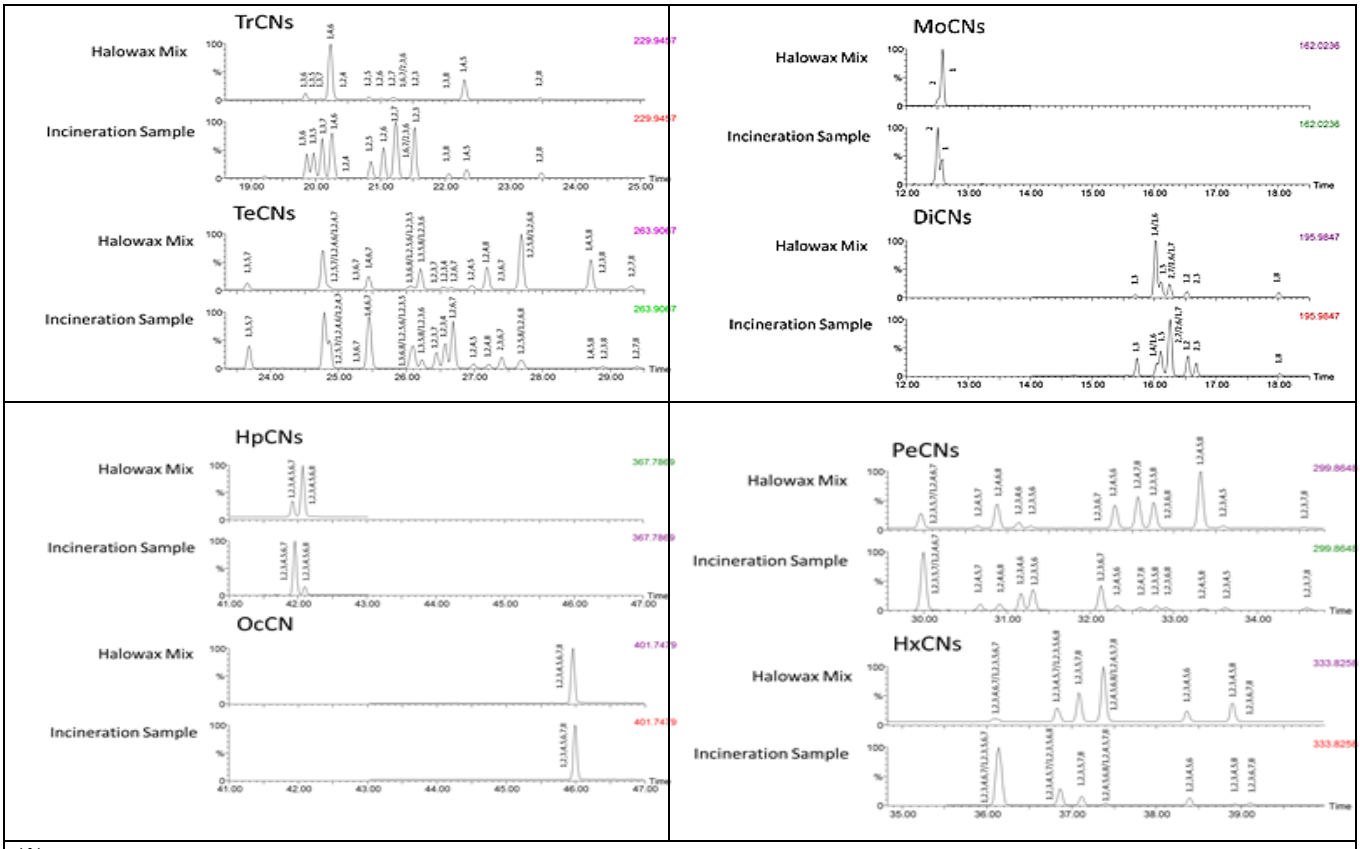
Up to now, not sufficient of $^{13}C_{10}$-PCN for internal standard, so alternatively used $^{13}C_{12}$- PCB

10 . Case studies of PCN screening in products and materials

Few countries or institutes have screened PCNs in goods, products, and waste. These case studies give initial insight into PCN contamination of several products and materials. The case studies are briefly described below with links to the reports/publications mentioned in the margin along with their web links where available.

10-1 Analysis of illegally imported technical PCNs

Polychlorinated naphthalene technical preparation was illegally imported from UK to Japan and evaluated for detailed content and profile of congeners. Principal component analysis (PCA) and cluster analysis of the PCN congeners with isomerization assessment of the homo-groups and the ratio of different homo-categories showed that the composition of the unknown mixture was similar to that of Halowax 1001. However, the detailed principal component analysis and cluster analysis showed that the imported PCNs were more Illegal [38]and were not matched with Halowax 1001 as the chlorine content of the imported PCN formulation (50-52%) was determined. Based on the chlorine content and distribution of congeners. It was concluded that the illicitly imported PCN mixture could be stock Seekay wax R93.



※Halowax Mix： Halowax 1000,1001,1013,1014,1031,1051,1099 mixture
Incineration sample：flue gas sample

Figure (4) : Chromatogram of PCN congeners from technical mixtures and waste incineration

10-2 Analysis of PCNs in PCBs

Yamashita et al [39] have investigated a wide range of technical mixtures of PCBs for PCN content. The PCB mixtures examined included: Aroclors 1016, 1232, 1248, 1254, 1260, 1262, Kanechlors 300, 400, 500, and 600 (KC-300, KC-400, KC-500 and KC-600), Clophens A40 and T64, Phenoclors 3,4,5, and 6 (DP3, DP4, DPS and DP6), Sovol, and Chlorofen.The levels of PCNs in the commercial PCB formulation were in the range of 39 to 730 mg/kg and Huang et al [40] recently analyzed the major Chinese PCB3 formulation and detected relatively high levels of PCN (1307 mg/kg).

10-3 Analysis of PCN and other UPOPs in by-product of chloromethane production[41]

High levels of unintended PCNs and other persistent organic pollutants (HCB, HCBD) are formed in the production of chlorinated solvents such as tetrachlorethylene, trichloroethylene, and dichloroethylene. The production of unintentionally produced POPs during methanol-based production of chlorinated methane has been investigated in China. High levels of Octachlornaphthalein, other PCNs, and other highly chlorinated compounds such as dichlorodiphenyl, octachlorosterene, hexachlorobutadiene, hexachlorobutadiene, hexachlorobenzene and pentachlorobenzene have been found in the production of carbon tetrachloride by methanol produced. The total amounts of emissions during the production of chlorinated methane in China from PCNs in 2010 were estimated at 427 kg[38]. In addition to significant amounts of HCH, HCB, PCB, PCN, OTC, PCB and BPH releases have been estimated[39] as 10080, 7350, 5210, 212, and 167 kg respectively. PCBs and polydioxins were also detected in the by-product. The total dioxin-like TTEs from chlorinated methane production in China in 2010 were estimated for PCNs to 563 g eq and for PCDD/PCDFs to 32.8 g eq

10-4 Monitoring of PCNs in rubber and different waste fractions[40]

Monitoring of PCNs was conducted in 21 rubber belts, 1 FB neoprene rubber and a batch of waste parts (rubber products, waste-derived fuels (RDF), automobile shredding residues (ASR) and fly ash). The patterns of PCNs were compared with 7 different halowax formulations. PCNs were also detected at different levels. The highest level was found in FB neoprene rubber [42].

11. Standards and approved methods of analysis

Methods for analyzing different types of POPs have been developed by ISO, CEC, EPA, AOAC and American Society for Testing Materials, DIN and JIS. Some examples of analytical methods for PCBs include:

Table (6): Standard methods for the detection of polychlorinated naphthalenes in oils, transformers, insulating fluids and petroleum products

M	method	The details
1-	EN 12766-1 (2000 .) method	Petroleum products and used oils - Identification of PCBs and related products - Part 1: Separation and identification of selected congeners of PCBs by gas chromatography using an electron capture detector.
2-	EN 12766-2 (2002 .) method	Petroleum products and oils used - Identification of PCBs and related products - Part 2: Calculation of PCB content
3-	Method (EN 61619 (1997 .)	Buffer fluids - contamination with polychlorinated biphenyls - determination method using gas chromatography by capillary column.
4-	EPA Method 8082	PCBs using gas chromatography (www.epa.gov/epaoswer/hazwaste/test/pdfs/8082.pdf).
5-	EPA Method 4020	Detection of PCBs using immunofluorescence
6-	Standard NBR No. 13882: 1997	Dielectric fluids - Determination of PCB content
7-	EPA Method 9079	Test method for the detection of PCBs in transformer oils (www.epa.gov/epaoswer/hazwaste/test/pdfs/9079.pdf);

Table (7): Methods for detecting polychlorinated naphthalene in solids

M	method	the details
1-	Method (EN 15308 (2008 .)	Waste characterization - Identification of selected PCBs in solid waste, using capillary gas chromatography with electron capture or mass spectrometry detection.
2-	EPA 8080 . method	Organochlorine pesticides and polychlorinated biphenyls
3-	Methods for checking general waste standards	For the examination of standards for public and privately controlled waste and industrial waste under special control, Notice No. 192 issued by the Japanese Ministry of Social Welfare and Labor on July 3, 1992.

Table (8): Methods for detecting polychlorinated naphthalenes in water, sludge, gases and others:

M	method	the details
1-	Method DIN 38414-20 (1996 .)	German standard methods for testing water, wastewater and sludge - sludge and sediment (Group S) - Part 20: Identification of 6 PCBs (P20).
2-	Method NVN 7376 (2004)	Leachation Characteristics - Determination of leaching of PAHs, PCBs, OCPs, EOX, phenols and cresols from building waste materials and homogeneous waste using diffusion test - earthy and solid stone materials.
3-	Method No. H 3-2 of the Norwegian Institute of Water Research	Determination of organochlorine compounds in sediments, water and biological materials by gas chromatography method
4-	Method (NVN 7350 (1997):	Leaching properties of earthen and solid masonry and waste materials - Leaching tests - Determination of leaching of PAHs, PCBs, and EOX from granular materials using a cascade test.
5-	Method NEN 7374 (2004)	Leachability Characteristics - Column test to determine the leaching of PAHs, PCBs, OCPs, EOXs, phenols and cresols from granular materials. Earthy and hard stone materials.
6-	JIS K 0093 (2006 .) method	Method for testing PCBs in industrial water and wastewater
7-	The method of the International Organization for Standardization (10382) 2002	Soil quality - Determination of organochlorine pesticides and polychlorinated biphenyls - Gas chromatography method with electron capture detection.
8-	ISO 6468 method (1996)	Water quality - Determination of specific organochlorine insecticides, PCBs and chlorobenzenes - Gas chromatography method after liquid-liquid extraction
9-	EPA Method 9078	Test method for polychlorinated biphenyls (PCBs) in soil
10-	EPA method 8275 thousand	For Semi-Volatile Organic Compounds (Polycyclic Aromatic Hydrocarbons and PCBs) in soil/slurry and solid waste using thermal extraction/gas chromatography/mass spectrometry, EPA Analytical Chemistry Guidelines SW-846
11-	EPA Method 1668, Revision A:	Chlorinated biphenyls congeners in water, soil, sediment, and tissues by HRGC/HRMS, US Office of Water, EPA No. 821-R-00-002, US EPA (4303) December 1999.
12-	Method (1948) 2006 EN	Emissions from stationery - Determination of the mass concentration of PCDD/PCDF and dioxin-like PCBs. Part 1: Sampling, Part 2: Extraction and clean-up of PCDD/PCDF, Part 3: Identification and quantification of PCDD/PCDF.
13	Method DIN 38414-20 (1996)	German standard methods for testing water, wastewater and sludge - sludge and sediment (Group S) - Part 20: Identification of 6 PCBs (P20).

11-1 Other ways

The International Electrotechnical Commission has developed methods for analyzing electrotechnical products for the identification of PBBs, as follows:

- IEC 62321 (2008) Electrotechnical Products - Determination of levels of the six regulated substances (lead, mercury, cadmium, hexavalent chromium, PBBs and PBDEs);
- Furthermore, useful knowledge can be obtained from the literature listed below on the method for analyzing different sources of PBBs:

- (B) US Agency for Toxic Substances and Disease Registry (2004). A brief overview of the toxicity of PBDEs and PBDEs;
- Kimlin S. et al. (2009) Brominated Flame Retardants in the European Chemicals Policy on Regulation and Determination of REACH in Substances, J. Kurmat A, 1216, 320-330.
- (D) Clark, B. et al (2008) PBDEs and PBDEs in Australian Sewage Sludge, Chemosphere, 73, 980-989.
- (e) Kovasi, A.; et al. (2003) Identification of BFRs, focusing on PBDEs in environmental and human samples--a review, Enferon International, 29, 735-756.

- (f) Henry Ann. et al. (2006) Presence of PBBs, PBDDs, and PBDFs as impurities in PBDE commercial mixtures, Environ Science and Technology, 40, 4405-4400.

For PCBs and PBBs, there may be particular interest in identifying dioxin-like PCBs and PBBs. To do this, internationally accepted methods such as those used for the analysis of PCDDs/PCDFs should be applied. For screening purposes, a test kit is available to determine the amount of PCBs in oils and soils (based on immunoassays or chlorine determination). If the result is negative, no confirmatory PCB analysis is necessary. If the result is positive, a confirmatory chemical analysis should be performed, or the waste may be considered as waste containing or contaminated with PCBs.

11-2 International standards for analysis of PCNs

There is currently no international standard for the analysis of PCNs in products.The only international standard methods approved for the analysis of PCNs in water have been developed by the International Organization for Standardization (ISO): ISO/TS 16780[42] .

12. Conclusion and recommendations

Experimental studies of screening and sampling methods confirm that samples of materials and instruments can be checked for chlorine in the field or in the laboratory. Greases, paints, rubber and cables, but there are still many analytical difficulties associated with the accurate determination of PCNs, and current methods are similar to the analytical methods used for PCBs. It relies on carbon cleaning (from arrays) and phase fractionation followed by high-resolution chromatography, and the use of high-resolution spectrographs to know the properties of mass (HRGC/HRMS) for the minimum levels of high selectivity among PCNs. However, less than half of the potential isotropic compounds are commercially available and isotopically labeled, eg there are no 13C-labelled trichloro-naphthalenes. Meanwhile, there are currently no congeners of 13C-labeled PCNs commercially available, and therefore 13C-labeled PCBs are frequently used as internal standards for analyzing PCNs. And since analytical chemistry is an important framework for examination and analysis, this study recommends further studies and clarification of what has not been clarified in this study in order to clarify simple and accessible methods of examination and analysis.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that they have no conficts of interest.

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